SOIL pH OVER TIME

by
Robert G. Stevens
Extension Soil Scientist
Irrigated Agriculture Research and Extension Center
Washington State University
Prosser, Wa. 99350

When dealing with soils as a component of our agricultural production system, we must be aware of their physical, biological and chemical properties. These properties determine the potential productivity of the soil and the management practices that will be necessary to obtain maximum yields. Soil reaction or acidity is one of the soil chemical properties that we must understand and manage for maximum production.

The soil reaction or acidity is generally reported as soil pH. The pH of the soils affects the availability of nutrients, the reaction of fertilizers with the soil, the microbial populations and activity, and root growth and function in the soil. Therefore, an understanding of your soil pH is essential for proper management.

Soil pH

The acidity or alkalinity of any solution is determined by the relative concentration of hydrogen (H^+) and hydroxyl (OH^-) ions in that solution. The acidity is generally defined by the pH of the solution. The pH is defined as the logarithm of the reciprocal of the H^+ ion concentration (activity), or symbolically,

$$pH = \log \frac{1}{H^+}$$

Therefore, as the concentration of H^+ ions in a solution increases the pH of the solutions decreases. When pure water dissociates or ionizes into H^+ and OH^- ion,

$$H_2O \quad H^+ + OH^-$$

the concentration of H^+ is .0000001 grams per liter or by definition pH = 7.0. The pH 7.0 is considered to be neutral. As the H^+ ion concentration increases the solution becomes acidic and the pH is below 7.0. As the concentration of H^+ decreases below .0000001 grams per liter the solution becomes alkaline and pH is above 7.0.

This Presentation is part of the Proceedings of the 1986 Washington State Potato Conference & Trade Fair.

The important factor to remember in the pH to H^+ relationship is that for every unit change in pH the H^+ ion concentration changes by a factor of ten. Therefore, if a pH 7 solutions drops to pH 6, then there has been a ten fold increase in the H^+ in solution. If the pH 7 solution dropped to pH 5, there would have been a 100 fold increase in H^+ concentration. Therefore, what may appear to be relative small changes in solution pH, may have a very large and significant change in the number of H^+ ions in solution.

In the soil system the pH of the soil solution is not the only factor affecting the acidity. Because of the negatively charged sites on the clays and organic matter in the soil, positively charged ions (cations) are adsorbed and held in reserve. These adsorbed cations are generally referred to as the exchangeable cations. The exchange capacity (CEC) of the soil is the soil's capacity to hold these cations. The base saturation of the soil refers then to the portion of the CEC filled with the basic cations calcium (Ca^{++}), magnesium (Mg^{++}), potasium (K^+) and sodium (Na^+). As the cations in solution are removed, cations adsorbed on the soil are released to replace them. As cations are added to the soil solution from outside sources such as fertilizers more of these cations are adsorbed replacing the cations already on the exchange sites. This relationship holds true for the H^+ ions in the soil system,

$$\text{Soil solid - } H^+ \rightleftharpoons \text{Solution } H^+$$

(Capacity)	(Intensity Factor)
(reserved acidity)	(pH)

Therefore, when the soil pH is modified, the solution H^+ and the H^+ ions held on the exchangeable positions on the soil solids must be considered.

Columbia Basin Soil pH

The virgin soils of the Columbia Basin are found to be neutral to alkaline in reaction. Because of the semi-arid climate of the region the soils have been only slightly weathered. However, the initiation, approximately thirty years ago, of intensive agriculture with its application of fertilizers and irrigation water has significantly changed the environment of these soils. With this change has come the expected change in soil chemistry and biology. Researchers have recently reported the general lowering of soil pH in wheat and pea fields of eastern Washington and northwestern Idaho (1). Orchard soils in central Washington have been decreasing in pH in the zone of fertilizer application for a number of years. The effect of fertilization on soil pH in Okanogan Valley soils in British Columbia was reported by Neilson and Hoyt (2). Growers and fertilizer dealers, as well as soil testing laboratories, in central Washington have reported an apparent general lowering of soil pHs across the area. However, to date a recent comprehensive survey of soil pH across central Washington has not been done.

A recent pH history for a number of fields in the Columbia Basin was supplied by F. L. Bair of Soiltest Farm Consultants, Inc., of Moses Lake, Washington. This data shows the general lowering of soil pH in some central Washington soils.

A comparison of 12 fields all on a Timmerman soil from a localized area of block 89 showed a decrease in the average pH of approximately 0.7 pH units from 7.03 to 6.30 (Table 1). These fields would have been slightly alkaline, pH 7.2-7.6, when irrigated farming started. The range in soil pH has also dropped. The distribution of soil pH showed none of the soils in the pH 6.0-6.4 range in 1977, with 7 of the 12 soils in this range by 1985 (Table 2). However, only one field had a pH below 6.0. Figure 1 shows the general lowering trend that occurred over the last 9 years for three of these Timmerman soils. One soil shows only a slight decrease, whereas the other two soils show a significant decrease in pH over time. Some of the year to year variability or fluctuation within fields might be expected since these samples represent random sampling of each field each year. This sampling would allow variability within the field to be seen. Changes in cultural practices may have also been responsible for some of the short term apparent pH increases during this period. The cultural history of these individual fields was not investigated.

A total of 21 fields on Ritzville soils from a localized area of block 47 were looked at for changes in soil pH from 1979 to 1985. Not all fields were sampled each year, and therefore some added variability may be seen in the average pH over time. These soils would have been neutral to slightly alkaline, pH 7.0 to 7.5, when placed under irrigation. In 1979, 20 fields had a pH range of 6.3 to 7.2 with an average pH of 6.65 (Table 3). In 1985, 19 soils had a slightly lower pH range of 5.8 to 7.1 with an average pH of 6.39. Nine of these fields were sampled in 1979, 1982, and 1985. The number of these nine fields with soil pH in the range of 6.0 to 6.4 had increased from 3 to 6, indicating a general lowering of pH. However, there were a number of soils in the pH 7.0 range that showed no significant change in pH during this time period. These Ritzville soils showed a wider range in pH response over time than did the Timmerman soils (Fig. 2). Of the three soils plotted, one showed no general change in pH, but considerable variability over time. The other two soils showed a similar downward trend in soil pH although they had started at different pH levels.

The comparison of the pH of these soils over time supports the concern that some of our Columbia Basin soils are experiencing a decrease in pH. However, they also point out the wide range in rate at which this pH decrease is occurring. Soils which still contain free calcium carbonate ($CaCO_3$) in the plow layer would not be expected to show a decreasing pH, because of their buffering capacity. Soils from these two locations indicate that most of the soil pH remain above 6.0, although they are significantly decreasing. However, soils from some areas, especially on sands, have been shown to have pH values below 5.5 in the surface 6 inches.

It can be concluded that many soils in the Columbia Basin are experiencing a gradual reduction in soil pH. The rate and degree of pH reduction will vary widely between fields depending upon soil characteristics and cultural practices.

Why Soils Become Acid

Soils decrease in pH and become acidic mainly because of leaching and the addition of H^+ ions to the soil. Crop removal of cations such as Ca^{++}, Mg^{++}, K^+, and Na^+ over time also lower soil pH.

Over irrigation leads to leaching of the basic cations (Ca^{++}, Mg^{++}, K^+, Na^+) from the crop rooting zone. Since these elements tend to keep the soil pH towards the neutral to alkaline side, the pH will become acid as the bases decrease relative to the amount of H^+ on the CEC. As the portion of basic cations decreases, they are replaced in the soil by the acidic cations H^+ and aluminum (Al^{+++}), which bring about additional lowering of the pH. This increases the difficulty in raising the soil pH, if necessary, because of this reserve acidity that replenishes or buffers the soil solution acidity.

The use of ammonium-type nitrogen fertilizers results in the acidification of the soil. When placed in the soils system the ammonium (NH_4^+) ion is microbially converted to the nitrate (NO_3^-) ion, through the process referred to as nitrification.

$$2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 2H_2O + 4H^+$$

$$2NO_2^- + O_2 \longrightarrow 2NO_3^-$$

In most soils this two step microbial process occurs very rapidly. The NO_3^- produced is then taken up by the plant and the H^+ ions are left behind to acidify the soil. The amount of acidity produced by each pound of nitrogen is surprisingly high. Table 5 provides this information for various ammonium-type nitrogen fertilizers. The amount of acidity formed is expressed as pounds of lime (calcium carbonate, $CaCO_3$) required to neutralize the acidity produced from 1 pound of nitrogen . As can be seen the sulfate and phosphate forms are significantly more acidifying than the other forms. This is because of the strong acids formed in the soil with the sulfate and phosphate ions following nitrification of the NH_4^+. Therefore, the amount of acidity added to the soil through nitrogen fertilization will depend on the source of the nitrogen and the amount added. Presently the only nonacidifying nitrogen source available is calcium nitrate. However, it is generally significantly more expensive than other sources.

Another significant source of H^+ ion addition comes with the addition of reduced forms of sulfur (S) to the soil. The most important type of reduced S in our rotations would probably be elemental S. When elemental S is applied to the soil it is microbially oxidized by Thiobacillus:

$$CO_2 + S + 1/2\ O_2 + H_2O \longrightarrow [CH_2O] + SO_4^{--} + 2H^+$$

This process produces H^+ ions in the presents of SO_4^{--} ions and is therefore very acidifying. Each 320 pounds of elemental S added to the soil will require approximately 1000 pounds of $CaCO_3$ to neutralize the acidity produced (3.1 lbs of $CaCO_3$ required per lb of S oxidized).

The question arises as to how much acidification is coming from our fertilization programs. If only the nitrogen component is considered, the effects of applying 400 lbs N/A to a potato crop can be seen in Table 6. If all the nitrogen is applied as $(NH_4)_2SO_4$ the maximum amount of acidification is produced, requiring 2,080 lbs of $CaCO_3$ to neutralize the acidity. As the amount of nitrogen applied as urea, ammonium nitrate or solution-N (20-0-0, 32-0-0) is increased the acidification is decreased down to a minimum of 720 lbs of $CaCO_3$. If any of the nitrogen is added in a phosphate form these values would need to be adjusted because phosphate forms are more acidifying than the straight nitrogen sources. From this it is apparent that the acidifying effect of nitrogen applied to a potato crop can be altered by both the nitrogen source and the rate applied. Sources such as $(NH_4)_2SO_4$ have an additional expense to be considered because of the increased acidification of soils where lower soil pH may be a potential problem.

This type of analysis can be expanded to consider a possible potato rotation. One possible rotation would be potatoes, corn, corn, wheat and wheat. With this rotation the possible acidification from nitrogen additions on all five crops could range from 2,610 to 3,970 lbs of $CaCO_3$ needed for neutralization (Table 7). These calculations assume that the nitrogen added to the corn and wheat crops required 1.8 lbs $CaCO_3$ per lb of N for a neutralization. These rough calculations suggest a need to add from 1 to 2 tons of lime per acre during this rotation to maintain the current soil pH. The acutal amount of lime needed to neutralize the fertilizer acidity would depend on the specific materials and rates used for a given rotation. The amount of acidification produced in this rotation would be enough with current management practices to continue the gradual decrease in soil pH. The addition of lime to neutralize the acidity added with fertilizer is a common practice in areas such as the midwest.

Effect of Lower Soil pH on Potatoes

The lowering of the soil pH below 6.0 may have several effects on potato production. The specific effect on a crop will depend on the soil and management practices being used. The effect on potato crops in the Columbia Basin has not been studied.

In many areas where alkaline soils occur, elemental S has been added to potato ground to lower the soil pH. Decreasing the soil pH has been found to cause a lower incidence of common scab. The specific reasons for this reduction in scab has not been determined. It may relate to a decrease in Ca^{++} levels, a change in the Ca^{++} to K^{+} ratios, Mn^{++} levels in solution or some yet to be determined relationship. The general lowering of pH in Columbia Basin soils may cause a reduction in scab, but this has yet to be documented.

Nutrient availability may also be affected by the gradual reduction of the soil pH. By the nature of the acidification process as the pH drops below 6.0 the Ca^{++} and Mg^{++} in the soil systems begins to decrease and may at some time become limiting.

However, since Columbia Basin soils still have a relative high base saturation, a Ca^{++} or Mg^{++} deficiency is not likely on most potato soils at this time. As the pH drops significantly below pH 6.0 available phosphorus begins to decrease. However, in our soils which are still dominated by calcium phosphate chemistry, phosphorus will not be effected until pH drops below 6.0 and aluminum and iron phosphate start becoming less available.

The rate of mineralization and nitrification will be decreased as pH drops below 6.0. The lower nitrification rates will cause nitrogen to remain for a longer time in the NH_4^+ form, thus reducing leaching loss. However, the supply of NO_3^--N to the plants may be decreased and may affect the diagnostic value of petiole NO_3^--N levels found, even though nitrogen may not be limiting.

As the soil pH drops to near 5.0 both Mn^{++} and Al^{+++} increase in concentration in the soil solution and reach toxic levels under specific conditions. Manganese toxicities have been noted in central Washington orchards with pH values below 5.5.

The major effect of lower soil pH may be on crops in the rotation other than potatoes. Legumes in the rotation may be especially subject to production problems. At pH values near 5.5 nodulation of many legumes such as alfalfa is inhibited. Decreased nodulation decreases symbiotic nitrogen fixation and thereby causes reduced stands and productivity. This effect on alfalfa has been documented by Rice (3) under very similar soil conditions to ours in Alberta, Canada. In northern Idaho decreased pea yields caused by acid soil have also been documented (1). Special attention must be given soil pH prior to establishing legumes. Other crops such as wheat and corn may be affected only early in the season when the roots are confined to the upper most acidic portion of the soil profile. A combination of a wet, cold spring and a soil pH below 5.5 may significantly slow early growth of these crops.

Future

Ammonium-type fertilizers will continue to be used as our major source of fertilizer nitrogen. Their economic advantages and supply dictate their continued use. Elemental sulfur and other forms of reduced sulfur will continue as part of our fertilizer mixes. Therefore, we will continue to acidify our soils and the pH of many soils will continue to be lowered. The depth to which acidification has occurred in the soil profile will also increase over time. As soil pH values approach the range below 6, crop responses will be noticed.

In an effort to minimize the rate of acidification over fertilization should be minimized. The loss of NO_3^--N from the root zone takes additional Ca^{++} and Mg^{++} with it, increasing acidification. Irrigation beyond crop needs should be minimized and managed to just cover leaching needed to prevent salt buildup in the soil profile.

Growers need to make an effort to monitor their pH over time to determine what affects their cultural practices are having. If their pHs are becoming questionably low the acidification of their fertilizer program should be minimized. If pH has reached a level where production of any crop is adversely affected liming can be considered. If the acidification is occurring below the plow layer where correction will be more difficult, liming should also be considered to prevent this. Most importantly the grower must gain an understanding of his soil and the specific requirements of his production system if he is to maintain profitable production.

REFERENCES

1. Mahler, R. L. and R. E. McDole. 1985. The influence of lime and phosphorus on crop production in northern Idaho. Communications in Soil Sci. Plant Analysis. 16(5):485-499.

2. Neilson, G. H. and P. B. Hoyt. 1982. Soil pH variation in British Columbia apple orchards. Can. J. Soil Sci. 62:695-698.

3. Rice, W. A., D. C. Penney, and M. Nyburg. 1977. Effects of soil acidity on rhizobia numbers, nodulation, and nitrogen fixation by alfalfa and red clover. Ca. J. Soil Sci. 57:197-203.

Table 1. The change in the range and average soil pH over time in 12 fields on Timmerman soil in block 89.

	pH	
Year	Range	X. (SD)
1977	6.5-7.3	7.03 (0.27)[1.]
1981	6.3-7.0	6.71 (0.23)
1985	5.9-6.7	6.30 (0.25)

1. Mean and standard deviation of 12 fields.

Table 2. Distribution of soil pH over time in 12 fields on Timmerman soil in block 89.

	pH Range			
Year	5.5-5.9	6.0-6.4	6.5-6.9	7.0-7.5
	No. of Fields			
1977	0	0	4	8
1981	0	3	8	1
1985	1	7	4	0

Table 3. The change in the range and average soil pH over time in fields on Ritzville soils in block 47.

		pH	
Year	# Fields	Range	X (SD)
1979	20	6.3-7.2	6.65 (0.39)
1982	11	6.2-6.9	6.47 (0.26)
1985	19	5.8-7.1	6.39 (0.49)

1. Mean and standard deviation for # of fields indicated.

Table 4. Distribution of soil pH over time in 9 fields on Ritzville soil in block 47.

	pH Range			
Year	5.5-5.9	6.0-6.4	6.5-6.9	7.0-7.5
	No. of Fields			
1979	0	3	4	2
1982	0	4	5	0
1985	0	6	0	3

Table 5. Pounds lime needed to neutralize acidity produced by 1 pound nitrogen from various ammonium nitrogen sources*.

Fertilizer material	% N	Lime needed/100 lbs material	Lime needed/lb of N applied
Ammonium nitrate (34-0-0)	34	62	1.8
Ammonium nitrate sulfate (30-0-0)	30	68	2.3
Monoammonium phosphate (11-48-0)	11	58	5.3
Ammonium phosphate sulfate (13-39-0)	13	69	5.3
Ammonium phosphate sulfate (16-20-0)	16	88	5.5
Ammonium phosphate nitrate (27-12-0)	27	75	2.8
Di-ammonium phosphate (18-48-0)	18	70	3.9
Ammonium sulfate (21-0-0)	21	110	5.2
Anhydrous ammonia (82-0-0)	82	148	1.8
Aqua ammonia (20-0-0)	20	36	1.8
Urea (46-0-0)	46	83	1.8

*From Western Fertilizer Handbook, 6th Edition (p. 94, 95).

Table 6. The acidity added with various fertilizer nitrogen combinations applied at a rate of 400 lbs N/A to a potato crop.

	Lbs lime for neutralization	
	Each Source	Total
$(NH_4)_2SO_4$	2080	2080
1/2 $(NH_4)_2SO_4$	1040	
1/2 Urea	360	1400
2/3 Urea	477	
1/3 Solution	243	720

Table 7. The acidity added with fertilizer nitrogen added in a possible potato rotation.

Crop	N lbs/A	Lbs lime for neutralization	
Potato	400	2080[1.]	720[2.]
Corn	300	540	540
Corn	300	540	540
Wheat	225	405	405
Wheat	225	405	405
Total	1450	3970	2610

1. Potato N as $(NH_4)_2SO_4$, other crops straight N sources.

2. All N applied as straignt N sources

Figure 1. The change in pH over time in three fields on Timmerman soil in block 89.

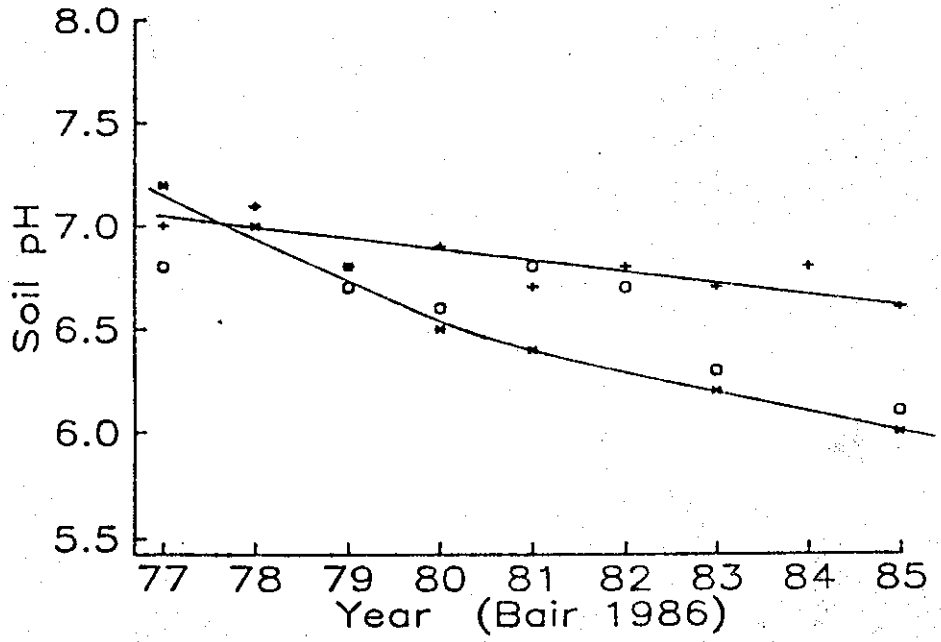
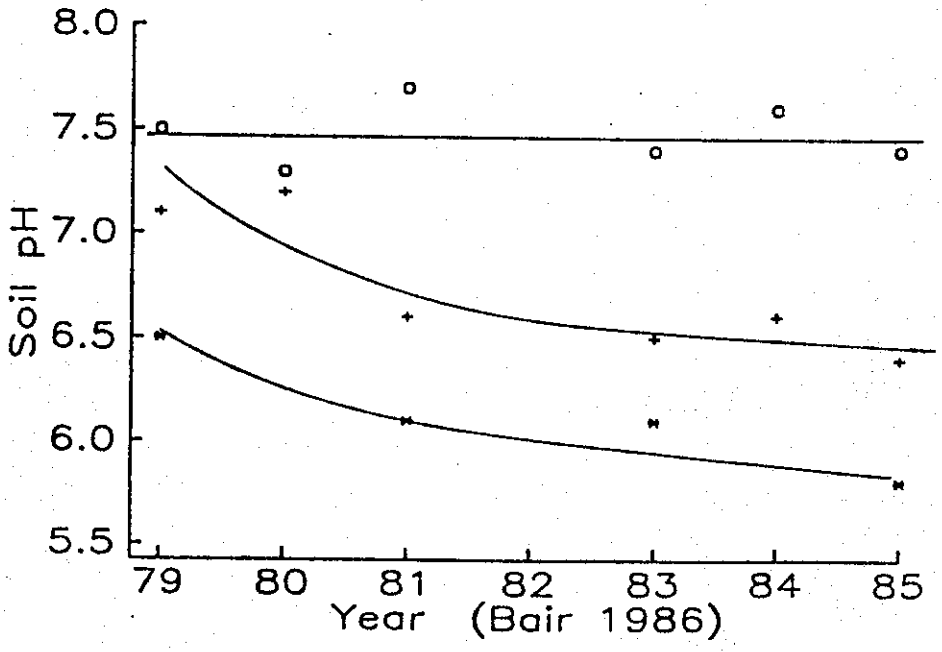
Figure 2. The change in pH over time in three fields on Ritzville soil in block 47.